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(21) International Application Number: PCT/US93/08833 (22) International Filing Date: 17 September 1993 (17.09.93) (30) Priority data: 07/954,539 29 September 1992 (29.09.92) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/ US]; 5200 Bayway Drive, Baytown, TX 77520 (US). (72) Inventors: BRANT, Patrick ; 103 Harborcrest, Seabrook, TX 77586 (US). CANICH, Jo, Ann, Marie ; 900 Hender- son Avenue, Apt. 808, Houston, TX 77058 (US). DIAS, Anthony, Jay ; 1411 Quite Green Court, Houston, TX 77062 (US). BAMBERGER, Robert, Lee ; 15903 Sea Palms, Crosby, TX 77532 (US). LICCIARDI, Gary, Frederick ; 20003 Big Timber, Humble, TX 77346 (US). HENRICH, Paul, Mark ; 2209 Maconda, Houston, TX 77027 (US).		(74) Agents: BUTTS, Evan, K. et al.; Exxon Chemical Com- pany, P.O. Box 5200, Baytown, TX 77522 (US). (81) Designated States: AU, CA, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: LONG CHAIN BRANCHED POLYMERS AND A PROCESS TO MAKE LONG CHAIN BRANCHED PO- LYMERS (57) Abstract A novel polymer and process for producing polymers incorporating linear long chain side branches are provided. The long chain linear branches occur at a frequency of less than 5.0 branches per 1000 carbon atom of the main polymer chains with at least some branches having a molecular weight greater than the critical molecular weight for entanglement of the polymer. The linear long chain branched polymers are produced by alpha-olefin macromolecule incorporation during bridged metallocene catalyst polymerization in solution and slurry processes. The polymers are characterized by superior processability characteristics of the polymer melts and superior mechanical characteristics of the solid polymers. The polymers are useful for fabrication into a wide variety of articles by conventional fabrication techniques.		

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TITLE

LONG CHAIN BRANCHED POLYMERS AND A PROCESS TO MAKE LONG
CHAIN BRANCHED POLYMERS

FIELD OF THE INVENTION

This invention relates to the field of long chain
branched polymers and a process to make them.

BACKGROUND OF THE INVENTION

This invention relates to novel polyolefin
polymers, processes for producing such polymers, and
applications for such polymers. The commercial
significance of polyolefin polymers is enhanced by the
variety of forms they may take which often exhibit
different physical properties. These different
properties make polyolefin polymers useful in many
different end use applications. The structural
features of polyolefins that are considered most
significant are molecular weight, which is related to
polymer chain length, the type and tacticity of side-
chain branches, and the distribution of side-chain
branches along the main polymer chains. Over the
years, considerable attention has been given to the
molecular architecture of polyolefins. Polyolefins can
be commercially produced using any one of a number of
processes. The random nature of most polymerization
processes results in a heterogeneous polymer, rather
than a truly homogeneous polymer product. Polyolefins
produced by classical Ziegler-Natta catalysts consist
of mixtures of molecules of different molecular weights
and different amounts of comonomer incorporation.
These differences result from the differences in
catalysts used, and differing rates of comonomer
incorporations. Other factors influencing polymer

products include choice of monomers, catalyst reactivity or ability to incorporate comonomers, and differing polymerization process conditions.

Commercial polyethylenes fall into one of two general categories, linear polyethylenes (LPEs) and "conventional" low density polyethylenes (LDPEs). LPEs are traditionally produced by addition polymerization of ethylene, or by the copolymerization of ethylene and an alpha-olefin comonomer, in a variety of processes using coordination catalysts. LDPEs are traditionally produced by free-radical polymerization of ethylene in high temperature and high pressure reactors using peroxide initiators. These two broad categories of polyethylenes have significant structural and physical differences. The most important difference between LPEs and LDPEs is the nature of the side-chain branching. LDPEs are highly side-chain branched having dendritic (tree-like) long chain side branches attached to the main polymer chains. These branches are created as a result of inter-molecular chain transfer during free-radical polymerization. Dendritic side-chain branching gives certain advantages, particularly processing advantages, to the polymer melts. However these processing advantages are balanced by disadvantages inherent with LDPEs relating to mechanical properties of the solid polymers such as lower stiffness, hardness, low tear resistance, low environmental stress crack resistance (ESCR) and, low tensile strength. These properties relative to LPEs with equivalent density and melt index properties.

Likewise, LPEs without long chain side branches have good mechanical properties such as good stiffness, hardness, tensile strength characteristics, tear resistance, and ESCR; however, from a processing standpoint, LPEs have the disadvantages of a tendency to melt fracture and low shear sensitivity resulting in

high melt viscosity, low melt strength and higher processing costs.

Polyethylene producers have spent considerable time and resources over the years trying to produce polymers possessing the polymer melt processing advantages of LDPEs and the mechanical properties advantages of solid LPEs. Most efforts have centered around adding long branches to LPEs. One conventional method of producing long chain branches in LPEs is to copolymerize ethylene with alpha-omega dienes. This method is illustrated in U.S. Patent 3,984,610, PCT application 91-17,194 and Japanese KOKAI 02-261,809, which are incorporated by reference herein.

In this method, dienes are simultaneously incorporated into propagating chains, thereby creating a covalent bridge between two linear molecules. The resulting structure in the vicinity of the bridge is typically shaped like the letter "H". The resultant side-chain branches can be long and are usually paired rather than isolated. As the number of dienes per molecule increases, the complexity of the branching approaches that of dendritic branching ultimately causing the polymer to lose its linear mechanical characteristics. In addition to mechanical properties shortcomings, polymers produced with dienes have encountered resistance to approval by regulatory authorities for food contact applications.

Other methods to produce long chain branches on LPEs involve post-polymerization treatments of linear molecules. Several different types of post-polymerization treatments have been used. United Kingdom Patent 901,148 demonstrates the production of branched polyethylene by treating molten polyethylene with oxygen. One method of doing this is by forcing air into the molten polyethylene during melt extrusion. This method of production results in non-linear long chain branches. United States Patent 4,586,995,

discloses the irradiation of molten polyethylene in the absence of oxygen to produce Y branches having two to fifty carbon chains per ten thousand carbon atoms in the main polymer chain. United Kingdom Patent

5 1,379,853 discloses the introduction of branches into polyethylene during the degradation of high density polyethylene in the presence of an organic peroxide. This process will result in dendritic side branches. Finally, Japanese Kokai 59-59,760 discusses the

10 production of long chain branched polyethylene by heating polyethylene containing a terminal vinyl group at 180° - 360°C under vacuum conditions or an inert atmosphere for five minutes to six hours. The polymer produced has long chain branches with a frequency of

15 3.5 branches per molecule. These branches are non-linear.

A third type of process for producing branching in linear polyethylene is the use of a polymerization cocatalyst which contains a long chain branched

20 polymeric group. U.S. Patent 4,500,648 and divisionals thereof disclose high density polyethylene production with branches prepared by polymerization of ethylene in the presence of a coordination catalyst containing an organoaluminum compound having a branched polymeric

25 hydrocarbyl group as one of its substituents. The polymers produced by this method contain non-linear long chain branches.

A method for the preparation of LLDPE using only ethylene is described in European Application Number

30 87108556.9 EPA 250,999. The method used is the oligomerization of ethylene using nickel based catalysts followed by copolymerization of the olefin mixture with ethylene through use of a chromium catalyst system. The objective of this application is

35 to utilize a process for preparing higher olefins to prepare a mixture of olefins which is then copolymerized to yield the LLDPE structure. The LLDPE

prepared in this method consists of polyethylene with a distribution of side-chains having 14 to 200 carbon atoms. One deficiency of this application is that it utilizes very low activity catalysts to form the oligomers and the subsequent copolymers. Secondly, this application does not recognize the importance of utilizing even longer side-chains than those described in the application.

A method for producing LLDPE containing long-chain branches is described in European patent application 91301811.5 EPA 446,013 and Japanese application H1-251748. EP 91301811.5 presents the polymerization of ethylene using Nickel complexes to give LLDPE containing long-chain branching. JP H1-251748 presents the copolymerization of ethylene and hexene using Nickel based polymerization catalysts. Using the catalyst systems described in the application, ethylene copolymers containing short and long chain branches are produced. The chief limitations of these applications are those known for Nickel based catalyst systems: 1) the low catalyst activities (30 g polymer/mmol catalyst in 1 hr); and 2) molecular weight distribution is proportional to molecular weight, therefore high molecular weights are accompanied by broad molecular weight distributions. This method does not produce higher Mw with narrow Mw/Mn.

SUMMARY OF THE INVENTION

This invention relates to novel polymers and processes for making polymers incorporating linear long chain side branches. The term "linear" is herein defined to include side chains that have some side chain branching but are not dendritic. The linear long chain branches are comprised of sidechains being at least 250 carbons long, which have molecular weights at least as great as the critical molecular weight for entanglement (M_C) of the polymer. The linear long

chain branches occur at a frequency of less than 5.0 branches per 1000 carbon atoms in the main polymer chains. The linear long chain branched polymers are produced by incorporating a macromolecule during
5 metallocene-catalyzed solution polymerization processes (solvent or bulk process at low, medium or high pressure). The long chain branched polymers possess the processability characteristics of conventional long chain branched polymer melts and the mechanical
10 characteristics of conventional solid linear polymers. Polymers produced in accordance with this invention are useful for fabrication into a wide variety of articles by injection molding, extrusion coating and molding, blown film, cast film, thermoforming and rotational
15 molding.

DETAILED DESCRIPTION OF THE INVENTION

During traditional coordination-catalyst polymerization of polyethylenes, most polymer chains
20 are terminated by the beta-abstraction mechanism which results in terminal unsaturation. If the molecule terminates after incorporation of a comonomer, the result is vinylene or vinylidene unsaturation. If the molecule terminates after the incorporation of
25 ethylene, the result is vinyl unsaturation. A vinyl unsaturated molecule can be considered a large alpha-olefin.

Linear copolymers are produced by additional polymerization of two or more vinyl terminated monomers
30 ranging in size from two to thirty carbon atoms. In the present invention, copolymers are produced in which vinyl terminated polymers, also called macromonomers or macromers, are incorporated into the addition polymerization reaction along with the monomers. The
35 vinyl terminated polymers responsible for the unique characteristics of polymers produced in accordance with the present invention are molecules having molecular

weights greater than the critical molecular weight for entanglement (M_c) of the polymer into which the vinyl terminated polymers are incorporated. The M_c for polyethylene is 3,800. The vinyl terminated polymers of this invention are 250 or more carbon atoms long, preferably 350 to 3500, even more preferably 300 to 3000, or have a Mw of greater than 6000. Further, the vinyl terminated polymers of this invention are incorporated into the growing polymer at an average frequency of no more than 5 long side chains per 1000 carbon atoms along the main chain, preferably the average frequency is 0.2 to 3 long side chains per 1000 carbon atoms, more preferably 0.9 to 2 long side chains per carbon atoms.

Using traditional coordination catalyst processes, these vinyl terminated polymers do not incorporate into growing polymer chains. The inventors have discovered that using certain metallocene catalysts, preferably under solution process conditions, in accordance with the present invention will result in these vinyl terminated polymers being incorporated into growing polymer chains at controllable amounts of incorporation. As these vinyl terminated polymers are incorporated into propagating polymer chains, they become isolated long chain branches of that polymer chain. The inventors have found that long chain branches, in accordance with the present invention, yield polymers having the positive mechanical attributes of solid linear polyolefins, while having the positive processing characteristics of melts of branched polyolefins.

The vinyl terminated polymers of this invention which eventually become side chains can be homopolymers or copolymers of one or more C_2 to C_{30} olefin, preferably alpha olefins, even more preferably homo or copolymers of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene and 4-methylpentene-1. Cyclic

olefins are also useful monomers in the practice of this invention. Likewise, the main chain can also be a homopolymer or copolymer of one or more C₂ to C₃₀ olefins, preferably alpha olefins, even more preferably homo or copolymers of ethylene, propylene, butene-1, pentene-1, hexene-1, octene-1 and 4-methyl-pentene-1. Copolymer is herein defined to include polymers of 2 to 4 different monomers and block copolymers of any of the above olefins or alpha olefins.

10 The vinyl terminated polymers useful in this invention can be prepared using a variety of metallocene catalysts and process conditions. The particular choice of catalyst and process conditions depends upon the desired polymer composition and
15 molecular weights. High vinyl termination content is necessarily preferred. Preferably about 0.9 to about 1.1 chain end unsaturations per macromer are present, even more preferably about 1 chain end unsaturation per macromer. Conditions which favor their formation are
20 high temperatures, no comonomer, no transfer agents like hydrogen, and a non-solution process or a dispersion using an alkane diluent. Thus the metallocene should be active at relatively high temperatures. The selected metallocene may also be
25 thermally activated to yield the beta-hydrogen eliminated product; vinyl ends. Thus one could prepare materials at low temperature then increase the temperature to get the beta-hydride eliminated product. The steric requirements of the metallocene will affect
30 the degree to which copolymerization occurs. Metallocenes which possess steric hindrance will yield vinyl terminated polymers which are relatively free of branches when compared to metallocenes which do not possess this hindrance.

35 Another method producing vinyl termination involves production of polymer with an ethylene "cap" or end with the needed vinyl group. This could be

accomplished by beginning polymerization at a low temperature, for example, below zero degrees Celsius, and raising the reaction temperature at the "end" of the reaction, for example, to above ten degrees

5 Celsius, and simultaneously adding ethylene so that the ethylene preferentially polymerizes to form an end "cap" or block. A block copolymer of ethylene and a C₃ to C₃₀ alpha olefin would also present the necessary vinyl termination.

10 The vinyl terminated polymers can be optimally copolymerized using metallocenes which are sterically unhindered. In addition the polymerization system should be a single-phase, or if two-phase, the vinyl terminated polymers must be sufficiently mobile to
15 permit their copolymerization. The preferred process for their copolymerization is a solution process. Thus the process solvent and temperature preferred are those in which the vinyl terminated polymer is soluble or substantially swollen.

20 The present invention preferably utilizes catalyst system comprising a metallocene catalyst with cocatalyst activators of an alumoxane or a "non-coordinating" anion. The metallocene catalyst is an activated cyclopentadienyl group 4 transition metal
25 compound. In particular, the metallocene catalysts employed in this invention are organometallic coordination compounds which are cyclopentadienyl derivatives of group 4 metals of the periodic table of the elements and include mono-, di- and tri-
30 cyclopentadienyls and their derivatives. Particularly desirable are the metallocenes of the group 4 metals: titanium, zirconium and hafnium. The cyclopentadienyl metallocenes of this invention can be activated with either an alumoxane or a "non-coordinating" anion-type
35 activator. In general at least one metallocene compound is employed in formation of the catalyst system. Metallocenes employed in accordance with this

invention contain at least one cyclopentadienyl ring and preferably comprise titanium, zirconium, or hafnium, most preferably hafnium, or zirconium for bis-cyclopentadienyl compounds and titanium for mono-cyclopentadienyl compounds. The cyclopentadienyl ring can be substituted or unsubstituted or contain one or more substituents e.g. from 1 to 5 substituents such as for example, hydrocarbyl substituent e.g. up to five C₁ to C₂₀ hydrocarbyl substituents or other substituents e.g. for example, a trialkyl cyclic substituent. A metallocene may contain 1, 2 or 3 cyclopentadienyl rings, however, two rings are preferred for use with hafnium or zirconium. One ring is preferred for use with titanium.

The catalyst system used in this invention can be described as comprising cyclopentadienyl transition metal catalyst having at least one delocalized pi-bonded moiety and an activating cocatalyst. The catalyst system used in this invention can also be described as comprising a cyclopentadienyl transition metal catalyst of a transition metal compound containing a single cyclopentadienyl group and a heteroatom containing group each bonded to the transition metal, said cyclopentadienyl group and heteroatom containing groups optionally bridged through a divalent moiety and an activating cocatalyst.

In another embodiment of the present invention the macromonomer can be polymerized in a gas phase process. This may be achieved by pre-polymerizing the macromonomer by one of many methods known in the art. For example, the method for supporting a catalyst known in U.S. Patent Application 885,170 filed 5-18-92, incorporated by reference, discloses how to place a catalyst on a support. This supported catalyst can then be combined with the macromonomer under appropriate polymerization conditions to pre-polymerize the macromonomer with the supported catalyst. This

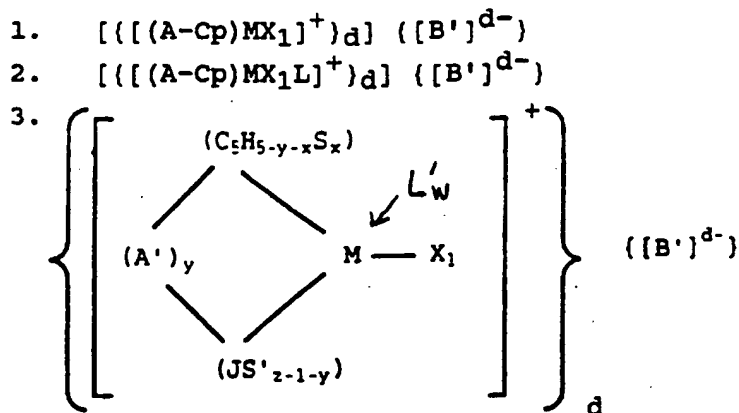
combination can then be introduced into a gas phase polymerization reactor to produce long chain branched polymers in this invention.

5 This macromonomer may also be pre-polymerized with other traditional gas phase supported catalysts and similarly introduced into the gas phase polymerization reactor. Likewise, one could use a two step process wherein the macromonomer or the catalyst is first placed on support using techniques known in the art and
10 then the catalyst and/or the macromonomer are added later to form the supported pre-polymerized catalyst combination. As is well known in the art, the pre-polymerization process is normally a slow, controlled process to initiate controlled polymer fracture or
15 support fracture thus, one of ordinary skill in the art would be sure to maintain appropriate reaction conditions such as temperatures from 40°C to 140°C in a suitable solvent with the introduction of ethylene, or suitable comonomers to form the macromonomers in a
20 controlled amount.

Ionic Catalyst System - General Description

The process of this invention is practiced with that class of ionic catalysts referred to, disclosed,
25 and described in European Patent Applications EP 0 277 003 A1 and EP 0 277 004 A1, and PCT Application WO 92/00333, and U.S. Patents 5,055,438 and 5,096,867, which are herein incorporated by reference. The ionic catalysts used in this invention can be represented by
30 one of the following general formulae (all references to groups being the new group notation of the Periodic Table of the Elements as described by Chemical and Engineering News, 63(5), 27, 1985):

12



wherein:

(A-Cp) is either (Cp) (Cp*) or Cp-A'-Cp*; Cp and Cp* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 element, substituted Group 16 element or halogen radicals, or Cp and Cp* are cyclopentadienyl rings in which any two adjacent S groups are joined forming a C4 to C20 ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp* rings or (C₅H₅-y-xS_x) and JS'(_{z-1-y}) groups;

(C₅H₅-y-xS_x) is a cyclopentadienyl ring substituted with from zero to five S radicals;

x is from 1 to 5 denoting the degree of substitution;

M is titanium, zirconium, or hafnium;

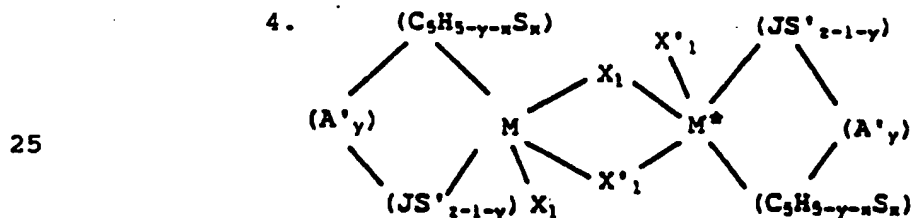
X₁ is a hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-

substituted organometalloid radical which radical may optionally be covalently bonded to both or either M and L or all or any M, S, or S';

(JS_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

y is 0 or 1;

L is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal center M and M* are bridged by X₁ and X'₁, wherein M* has the same meaning as M and X'₁ has the same meaning as X₁ where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by the formula:



w is an integer from 0 to 3;

B is a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 angstroms or an anionic Lewis-acid activator resulting from the reaction of a Lewis-acid activator with the precursor to the cationic portion of the catalyst system described in formulae 1-4. When B' is a Lewis-acid activator, X₁ can also be an alkyl group donated by the Lewis-acid activator; and

d is an integer representing the charge of B.

The improved catalysts are preferably prepared by combining at least two components. In one preferred method, the first component is a cyclopentadienyl derivative of a Group 4 metal compound containing at least one ligand which will combine with the second component or at least a portion thereof such as a cation portion thereof. The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained in said Group 4 metal compound (first component) and a non-coordinating anion which is either a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom or an anion comprising a plurality of boron atoms such as polyhedral boranes, carboranes and metallocarboranes.

In general, suitable anions for the second component may be any stable and bulky anionic complex having the following molecular attributes: 1) the anion should have a molecular diameter greater than 4 Å; 2) the anion should form stable ammonium salts; 3) the negative charge on the anion should be delocalized over the framework of the anion or be localized within the core of the anion; 4) the anion should be a relatively poor nucleophile; and 5) the anion should not be a powerful reducing or oxidizing agent. Anions meeting these criteria - such as polynuclear boranes, carboranes, metallocarboranes, polyoxoanions and anionic coordination complexes are well described in the chemical literature.

The cation portion of the second component may comprise Bronsted acids such as protons or protonated Lewis bases or may comprise reducible Lewis acids such as ferricinium, tropylium, triphenylcarbenium or silver cations.

In another preferred method, the second component is a Lewis-acid complex which will react with at least one ligand of the first component, thereby forming an ionic species described in formulae 1-4 with the ligand abstracted from the first component now bound to the second component. Alumoxanes and especially methylalumoxane, the product formed from the reaction of trimethylaluminum in an aliphatic or aromatic hydrocarbon with stoichiometric quantities of water, are particularly preferred Lewis-acid second components.

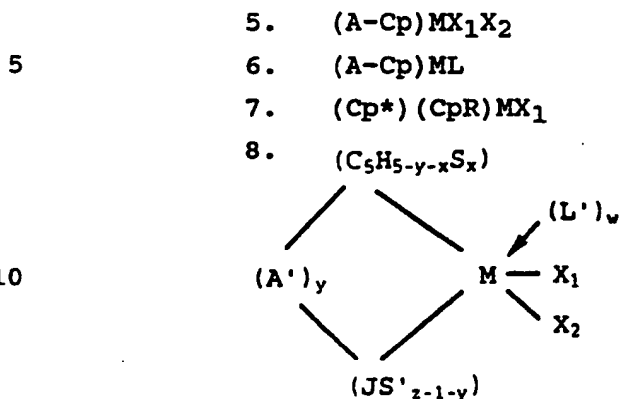
Upon combination of the first and second components, the second component reacts with one of the ligands of the first component, thereby generating an ion pair consisting of a Group 4 metal cation and the aforementioned anion, which anion is compatible with and "non-coordinating" toward the Group 4 metal cation formed from the first component. The anion of the second compound must be capable of stabilizing the Group 4 metal cation's ability to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization. The catalysts of this invention may be supported. U.S. Patents 4,808,561, issued 2-28-89; 4,897,455 issued 1-3-90; 5,057,475 issued 10-15-91; and U.S. Patent Application 459,921 (published as PCT International publication WO 91/09882) disclose such supported catalysts and the methods to produce such and are herein incorporated by reference.

A. The Metallocene Component

The Group 4 metal compounds; i.e., titanium, zirconium, and hafnium metallocene compounds, useful as first compounds in the preparation of the improved catalyst of this invention are cyclopentadienyl derivatives of titanium, zirconium and hafnium. In

16

general, useful titanocenes, zirconocenes, and hafnocenes may be represented by the following general formulae:



wherein:

- 15 $(A-Cp)$ is either $(Cp)(Cp^*)$ or $Cp-A'-Cp^*$; Cp and Cp^* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S , each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 elements, substituted Group 16 elements or halogen radicals, or Cp and Cp^* are
- 20 cyclopentadienyl rings in which any two adjacent S groups are joined forming a C_4 to C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

30 R is a substituent on one of the cyclopentadienyl radicals which is also bonded to the metal atom;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp^* rings or $(C_5H_5-y-xS_x)$ and $JS'_{(z-1-y)}$ groups;

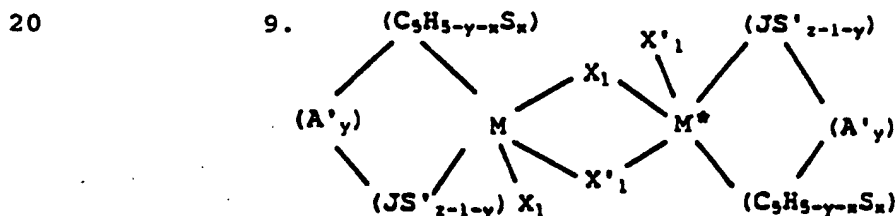
y is 0 or 1;

35 $(C_5H_5-y-xS_x)$ is a cyclopentadienyl ring substituted with from zero to five S radicals;

x is from 1 to 5 denoting the degree of substitution;

(JS_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2, S is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

L is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal centers M and M* are bridged by X₁ and X'₁, wherein M* has the same meaning as M and X'₁ has the same meaning as X₁ where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by formula 4;



wherein:

w is an integer from 0 to 3; and

X₁ and X₂ are, independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted Group 15 element radicals, or substituted Group 16 element radicals; or X₁ and X₂ are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or X₁ and X₂ together can be an olefin, diolefin or aryne ligand; or when

Lewis-acid activators are used, X_1 and X_2 can also be joined to form an anionic chelating ligand or can independently be any mono-valent anionic ligand including halides.

5 Table 1 depicts representative constituent moieties for the metallocene components of formulae 6-9. The list is for illustrative purposes only and should not be construed to be limiting in any way. A number of final components may be formed by permuting
10 all possible combinations of the constituent moieties with each other. Illustrative compounds of the formula 6 type are: bis(cyclopentadienyl)hafnium dimethyl, ethylenebis(tetrahydroindenyl)zirconium dihydride, bis(pentamethyl)zirconium ethylidene, dimethylsilyl(1-
15 fluorenyl)(cyclopentadienyl)titanium dichloride and the like. Illustrative compounds of the formula 7 type are: bis(cyclopentadienyl) (1,3-butadiene(zirconium), bis(cyclopentadienyl) (2,3-dimethyl-1,3-butadiene) zirconium, bis(pentamethylcyclopentadienyl) (benzene)
20 zirconium, bis(pentamethylcyclopentadienyl) titanium ethylene and the like. Illustrative compounds of the formula 8 type are: (pentamethylcyclopentadienyl) (tetramethylcyclopentadienylmethylene) zirconium hydride, (pentamethylcyclopentadienyl)
25 (tetramethylcyclopentadienyl)- (tetramethylcyclopentadienylmethylene) zirconium phenyl and the like. Illustrative compounds of the formula 9 type are: dimethylsilyl(tetramethylcyclopentadienyl) (t-butylamido)zirconium dichloride,
30 ethylene(methylcyclopentadienyl) (phenylamido)titanium dimethyl, methylphenylsilyl(indenyl) (phenylphosphido)hafnium dihydride and (pentamethylcyclopentadienyl) (di-t-butylamido)hafnium dimethoxide.

For illustrative purposes, the above compounds and those permuted from Table 1 include the neutral Lewis base ligand (L'). The conditions under which complexes containing neutral Lewis base ligands such as ether or those which form dimeric compounds is determined by the steric bulk of the ligands about the metal center. For example, the t-butyl group in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$ has greater steric requirements than the phenyl group in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NPh})\text{ZrCl}_2\text{Et}_2\text{O}$ thereby not permitting ether coordination in the former compound in its solid state. Similarly, due to the decreased steric bulk of the trimethylsilylcyclopentadienyl group in $[\text{Me}_2\text{Si}(\text{Me}_3\text{SiC}_5\text{H}_3)(\text{N-t-Bu})\text{ZrCl}_2]_2$ versus that of the tetramethylcyclopentadienyl group in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$, the former compound is dimeric and the latter is not.

TABLE 1

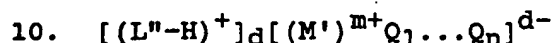
(A')	(C ₅ H ₅ -x-X) ₅ X	(3S', 3S'-1-v)	(B - Lewis Acid)	X ₁ or X ₂	M
dimethylsilyl	cyclopentadienyl	t-butylamido	hydride		zirconium
diethylsilyl	3,4-dimethylcyclopentadienyl	phenylamido	methyl		hafnium
di-n-propylsilyl	2,5-dimethylcyclopentadienyl	p-cylohexylamido	ethyl		titanium
di-isopropylsilyl	2-indenyl	p-cylohexylamido	phenyl		
di-n-butylsilyl	3,4-diethylcyclopentadienyl	perfluorophenylamido	n-propyl		
di-t-butylsilyl	2,5-diethylcyclopentadienyl	n-butylamido	isopropyl		
di-n-hexylsilyl	tetramethylcyclopentadienyl	methylamido	n-butyl		
methylphenylsilyl	tetraethylcyclopentadienyl	ethylamido	amyl		
ethylmethylsilyl	tetraphenylcyclopentadienyl	n-propylamido	isoamyl		ethylene
diphenylsilyl	tetra-n-propylcyclopentadienyl	isopropylamido	hexyl		propylene
di(p-t-butylphenethylsilyl)	3,4-di-n-butylcyclopentadienyl	benzylamido	isobutyl		1-butene
n-hexylmethylsilyl	3,4-dicyclohexylcyclopentadienyl	cyclohexylamido	heptyl		1,4-hexadiene
cyclopentamethylenesilyl	2,5-di-n-butylcyclopentadienyl	s-butylamido	octyl		1,3-butadiene
cyclooctamethylenesilyl	2,5-dicyclohexylcyclopentadienyl	t-butylphosphido	nonyl		1,3-hexadiene
cyclotrimethylenesilyl	3-n-octyl-4-n-hexylcyclopentadienyl	ethylphosphido	decyl		acetylene
dimethylgermanyl	2-tetrahydroindenyl	phenylphosphido	cetyl		methylacetylene
diethylgermanyl	3-ethyl-4-n-propylcyclopentadienyl	cyclohexylphosphido	chloro		benzynes
phenylamido	3-isopropyl-4-t-butylcyclopentadienyl	oxo	fluoro		diethylether
t-butylamido	3-phenyl-4-benzylcyclopentadienyl	methoxide	iodo		dimethylether
methylamido	3,4-diphenylcyclopentadienyl	ethoxide	methoxy		trimethylamine
t-butylphosphido	2,5-diphenylcyclopentadienyl	methylthio	ethoxy		triethylamine
ethylphosphido	3,4-bis(trimethylsilyl)cyclopentadienyl	ethylthio	propoxy		triphenyl-phosphine
phenylphosphido	bis(trimethylgermyl)cyclopentadienyl	dimethylamido	butoxy		phosphine
methylene	3,4-bis(trimethylstannyl)cyclopentadienyl	diphenylamido	phenoxy		tetrahydrofuran
dimethylmethylene	3,4-bis(triethylplumbyl)cyclopentadienyl	methylphenylamido	dimethylamido		thiophene
diethylmethylene	2-ethyl-5-n-propylcyclopentadienyl	dicyclohexylphosphido	methylamido		dimethylsulfide
dipropylethylene	2-methyl-5-t-butylcyclopentadienyl	diphenylphosphido	methylethylamido		
propylene	2,5-bis(trifluoromethyl)cyclopentadienyl	bis(trimethylsilyl)-amido	diphenylamido		
dimethylpropylene	3,4-bis(trimethylsilyl)cyclopentadienyl	trimethylsilyloxide	dicyclohexylphosphido		
diethylpropylene	3,4-bis(N,N-dimethylamido)-cyclopentadienyl		dimethylphosphido		
1,1-dimethyl-3,3-dimethyl	3,4-bis(dimethylphosphido)-cyclopentadienyl		ethyleneglycol dianion (both X)		
propylene	3,4-dimethoxycyclopentadienyl		methylidene (both X)		
tetramethyldisiloxane	2,5-dimethoxycyclopentadienyl		ethylidene (both X)		
1,1,4,4-tetramethyldisilyl	2,5-dimethyl-3,4-diethylcyclopentadienyl		propylidene (both X)		
ethylene	2,5-diethyl-3,4-dimethylcyclopentadienyl				
	2,5-dimethyl-3,4-di-t-butylcyclopentadienyl				

B. The Activator Component

Ionic catalysts can be prepared by reacting a transition metal compound with some neutral Lewis acids, such as $B(C_6F_6)_3$ or an alumoxane, which upon
 5 reaction with the hydrolyzable ligand (X) of the transition metal compound forms an anion, such as $([B(C_6F_5)_3(X)]^-)$, which stabilizes the cationic transition metal species generated by the reaction. Ionic catalysts can be, and preferably are,
 10 prepared with activator components which are ionic compounds or compositions.

Compounds useful as an activator component in the preparation of the ionic catalyst systems used in the process of this invention comprise a cation, which is
 15 preferably a Bronsted acid capable of donating a proton, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4 cation) which is formed when the two compounds are
 20 combined and said anion will be sufficiently labile to be displaced by olefinic diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Two classes of compatible non-coordinating anions have been disclosed
 25 in copending U.S. Patent Application Nos. 133,052 and 133,480: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a
 30 plurality of boron atoms such as carboranes, metallacarboranes and boranes.

In general, the activator compounds containing single anionic coordination complexes which are useful in this invention may be represented by the following
 35 general formula:



wherein:

H is a hydrogen atom;

[L"-H] is a Bronsted acid;

M' is a metal or metalloid;

Q₁ to Q_n are, independently, bridged or unbridged
5 hydride radicals, dialkylamido radicals, alkoxide and
aryloxy radicals, hydrocarbyl and substituted-
hydrocarbyl radicals, halocarbyl and substituted-
halocarbyl radicals and hydrocarbyl and halocarbyl-
substituted organometalloid radicals and any one, but
10 not more than one, of Q₁ to Q_n may be a halide radical;

m is an integer representing the formal valence
charge of M; and

n is the total number of ligands q.

As indicated above, any metal or metalloid capable of
15 forming an anionic complex which is stable in water may
be used or contained in the anion of the second
compound. Suitable metals, then, include, but are not
limited to, aluminum, gold, platinum and the like.
Suitable metalloids include, but are not limited to,
20 boron, phosphorus, silicon and the like. Compounds
containing anions which comprise coordination complexes
containing a single metal or metalloid atom are, of
course, well known and many, particularly such
compounds containing a single boron atom in the anion
25 portion, are available commercially. In light of this,
salts containing anions comprising a coordination
complex containing a single boron atom are preferred.

The preferred activator compounds comprising boron
may be represented by the following general formula:

30 11. $[L''-H]^+[BAr_1Ar_2X_3X_4]^-$

wherein:

B is a boron in a valence state of 3;

Ar₁ and Ar₂ are the same or different aromatic or
substituted-aromatic hydrocarbon radicals containing
35 from about 6 to about 20 carbon atoms and may be linked
to each other through a stable bridging group; and

X_3 and X_4 are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals, hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted Group 15 element radicals, substituted Group 16 element radicals and halide radicals, with the proviso that X_3 and X_4 will not be halide at the same time.

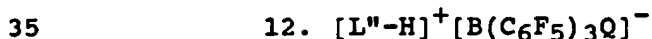
In general, Ar_1 and Ar_2 may, independently, be any aromatic or substituted-aromatic hydrocarbon radical. Suitable aromatic radicals include, but are not limited to, phenyl, naphthyl and anthracenyl radicals. Suitable substituents on the substituted-aromatic hydrocarbon radicals, include, but are not necessarily limited to, hydrocarbyl radicals, organometalloid radicals, alkoxy and aryloxy radicals, alkylamido radicals, fluorocarbyl and fluorohydrocarbyl radicals and the like such as those useful as X_3 and X_4 . The substituent may be ortho, meta or para, relative to the carbon atoms bonded to the boron atom. When either or both X_3 and X_4 are a hydrocarbyl radical, each may be the same or a different aromatic or substituted-aromatic radical as are Ar_1 and Ar_2 , or the same may be a straight or branched alkyl, alkenyl or alkynyl radical, a cyclic hydrocarbon radical or an alkyl-substituted cyclic hydrocarbon radical. X_3 and X_4 may also, independently be alkoxy or dialkylamido radicals wherein the alkyl portion of said alkoxy and dialkylamido radicals, hydrocarbyl radicals and organometalloid radicals and the like. As indicated above, Ar_1 and Ar_2 could be linked to either X_3 or X_4 . Finally, X_3 and X_4 may also be linked to each other through a suitable bridging group.

Illustrative, but non-limiting, examples of boron compounds which may be used as an activator component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such

as triethylammonium tetra(phenyl)boron,
 tripropylammonium tetra(phenyl)boron, tri(n-
 butyl)ammonium tetra(phenyl)boron, trimethylammonium
 tetra(p-tolyl)boron, trimethylammonium tetra(o-
 5 tolyl)boron, tributylammonium
 tetra(pentafluorophenyl)boron, tripropylammonium
 tetra(o,p-dimethylphenyl)boron, tributylammonium te-
 tra(m,m-dimethylphenyl)boron, tributylammoniumtetra(p-
 tri-fluoromethylphenyl)boron, tri(n-butyl)ammonium
 10 tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium
 salts such as N,N-dimethylanilinium
 tetra(pentafluorophenyl)boron, N,N-diethylanilinium
 tetra(phenyl)boron, N,N-2,4,5-pentamethylanilinium
 tetra(phenyl)boron and the like; dialkyl ammonium salts
 15 such as di(i-propyl)ammonium
 tetra(pentafluorophenyl)boron, dicyclohexylammonium
 tetra(phenyl)boron and the like; and triaryl
 phosphonium salts such as triphenylphosphonium
 tetra(phenyl)boron, tri(methylphenyl)phosphonium
 20 tetra(phenyl)boron, tri(dimethylphenyl)phosphonium
 tetra(phenyl)boron and the like.

Similar lists of suitable compounds containing
 other metals and metalloids which are useful as
 activator components may be made, but such lists are
 25 not deemed necessary to a complete disclosure. In this
 regard, it should be noted that the foregoing list is
 not intended to be exhaustive and that other useful
 boron compounds as well as useful compounds containing
 other metals or metalloids would be readily apparent to
 30 those skilled in the art from the foregoing general
 equations.

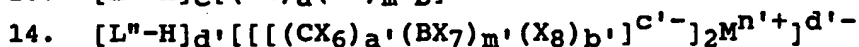
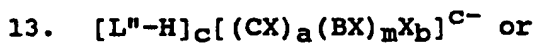
The most preferred activator compounds comprising
 boron may be represented by the following general
 formula:



wherein:

F is fluorine, C is carbon and B, L', and Q are defined hereinabove. Illustrative but not limiting, examples of most preferred activator compounds comprising boron which may be used in the preparation of the improved catalysts of this invention include N,N-dialkylanilinium salts (L' = N,N-dialkylaniline) where Q is a simple hydrocarbyl such as methyl, butyl, cyclohexyl, or phenyl or where Q is a polymeric hydrocarbyl of indefinite chain length such as polystyrene, polyisoprene, or poly-paramethylstyrene. Polymeric Q substituents on the most preferred anion offer the advantage of providing a highly soluble ion-exchange activator component and final ionic catalyst. Soluble catalysts and/or precursors are often preferred over insoluble waxes, oils, phases, or solids because they can be diluted to a desired concentration and can be transferred easily using simple equipment in commercial processes.

Activator components based on anions which contain a plurality of boron atoms may be represented by the following general formulae:



wherein

[L''-H] is either H⁺ or a Bronsted acid derived from the protonation of a neutral Lewis base;

X, X', X'', X₆, X₇ and X₈ are, independently, hydride radicals, halide radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals, halocarbyl radicals, substituted-halocarbyl radicals, or hydrocarbyl- or halocarbyl-substituted organometalloid radicals;

M is a transition metal;

a and b are integers ≥ 0 ; c is an integer ≥ 1 ;
 $a+a'+a''+c$ = an even-numbered integer from 2 to about 8;
 and m is an integer ranging from 5 to about 22;

a and b are the same or a different integer 0; c is an integer ≥ 2 ; $a + b + c =$ an even-numbered integer from 4 to about 8; m is an integer from 6 to about 12; n is an integer such that $2ca - na = d$; and d is an integer ≥ 1 .

Preferred anions of this invention comprising a plurality of boron atoms comprise:

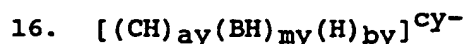
(1) A trisubstituted ammonium salt of a borane or carborane anion satisfying the general formula:



wherein:

ax is either 0 or 1; cx is either 1 or 2; $ax + cx = 2$; and bx is an integer ranging from about 10 to 12;

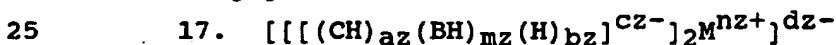
(2) A trisubstituted ammonium salt of a borane or carborane or a neutral borane or carborane compound satisfying the general formula:



wherein:

ay is an integer from 0 to 2; by is an integer from 0 to 3; cy is an integer from 0 to 3; $ay + by + cy = 4$; and my is an integer from about 9 to about 18; or

(3) A trisubstituted ammonium salt of a metallaborane or metallocarborane anion satisfying the following general formula:



wherein:

az is an integer from 0 to 2; bz is an integer from 0 to 2; cz is either 2 or 3; mz is an integer from about 9 to 11; $az + bz + cz = 4$; and nz and dz are, respectively, 2 and 2 or 3 and 1.

Illustrative, but not limiting, examples of second components which can be used in preparing catalyst systems utilized in the process of this invention wherein the anion of the second component contains a plurality of boron atoms (as in formulae 10-17) are mono-, di-, trialkylammonium and phosphonium and dialkylarylammonium and -phosphonium salts such as

bis[tri(n-butyl)ammonium] dodecaborate, bis[tri(n-butyl)ammonium]decachlorododecaborate, tri(n-butyl)ammonium dodecachlorododecaborate, tri(n-butyl)ammonium 1-carbadecaborate, tri(n-butyl)ammonium 1-carbaundecaborate, tri(n-butyl)ammonium 1-carbadodecaborate, tri(n-butyl)ammonium 1-trimethylsilyl-1-carbadecaborate, tri(n-butyl)ammonium dibromo-1-carbadodecaborate; borane and carborane complexes and salts of borane and carborane anions such as decaborane(14), 7,8-dicarbaundecaborane(13), 2,7-dicarbaundecaborane(13), undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane, tri(n-butyl)ammonium 6-carbadecaborate(12), tri(n-butyl)ammonium 7-carbaundecaborate, tri(n-butyl)ammonium 7,8-dicarbaundecaborate and metallaborane anions such as tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbazonaborate)cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaunaborato)nikelate(III), tri(n-butyl)ammonium bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium bis(tribromooctahydrido-7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)ammonium bis(undecahydridodicarbadodecaborato)cobaltate(III) and bis[tri(n-butyl)ammonium]bis(undecahydrido-7-carbaundecaborato)cobaltate(III). A similar list of representative phosphonium compounds can be recited as illustrative second compounds, but for the sake of brevity, it is simply noted that the phosphonium and substituted-phosphonium salts corresponding to the listed ammonium and substituted-ammonium salts could be used as second compounds in the present invention.

The preferred activator compounds comprising Lewis-acid activators and in particular alumoxanes are represented by the following general formulae:

18. $(R^3-Al-O)_p$
19. $R^4(R^5-Al-O)_p-AlR^6_2$
20. $(M')^{m+}Q'^m$

An alumoxane is generally a mixture of both the linear and cyclic compounds. In the general alumoxane formula, R^3 , R^4 , R^5 and R^6 are, independently a C_1-C_6 alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "p" is an integer from 1 to about 50. Most preferably, R^3 , R^4 , R^5 and R^6 are, each methyl and "p" is a least 4. When an alkyl aluminum halide is employed in the preparation of the alumoxane, one or more R^{3-6} groups may be halide. M' and M are as described previously and Q' is a partially or fully fluorinated hydrocarbyl.

As is now well known, alumoxanes can be prepared by various procedures. For example, a trialkyl aluminum may be reacted with water, in the form of a moist inert organic solvent; or the trialkyl aluminum may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. Generally, however prepared, the reaction of a trialkyl aluminum with a limited amount of water yields a mixture of both linear and cyclic species of alumoxane.

Suitable alumoxanes which may be utilized in the catalyst systems of this invention are those prepared by the hydrolysis of a trialkylaluminum, such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, dimethylaluminum chloride, diisobutylaluminum chloride, diethylaluminum chloride and the like. The most preferred alumoxane for use is methylalumoxane (MAO). Methylalumoxanes having an average degree of oligomerization of from 4 to 25 ("p")

= 4 to 25), with a range of 13 to 25 are the most preferred.

It is recognized that an alumoxane is not a discrete material. A typical alumoxane will contain
5 free trisubstituted or trialkyl aluminum, bound trisubstituted or trialkyl aluminum, and alumoxane molecules of varying degree of oligomerization. Those methylalumoxanes most preferred contain lower levels of trimethylaluminum. Lower levels of trimethylaluminum
10 can be achieved by reaction of the trimethylaluminum with a Lewis base or by vacuum distillation of the trimethyl aluminum or any other means known in the art.

It is also recognized that after reaction with the transition metal compound, some alumoxane molecules
15 are in the anionic form as represented by equations 1-3, and thus for our purposes, are considered "non-coordinating" anions.

The activator compositions most preferred for forming the ionic catalyst used in this process are
20 those containing a tetrapentafluorophenyl boron anion; two or more tripentafluorophenyl boron anion groups covalently bond to a central atomic molecular or polymeric complex or particle; tripentafluorophenyl boron; or methylalumoxane.

25 Other examples of activator specific compositions which may be used to form an anionic catalyst useful in this invention are identified and more fully described in European Patent Application Nos. 0 277 003 and 0 277 004 and WO 92/00333 which are hereby incorporated by
30 reference.

CHOICE OF CATALYST

This invention relates to a process to produce long chain branched polymers, to catalysts used to
35 produce long chain branched polymers and to the polymers themselves. This invention relates to a method for producing polymers with substantially linear

long chain branching comprising contacting, under polymerization conditions, a vinyl terminated polymer (macromonomer) with a chain length of 250 or more carbons, with one or more olefin monomers and a

5 metallocene catalyst system comprising a mono, di, or tri cyclopentadienyl transition metal catalyst cocatalized with a non-coordinating anion or an alumoxane or a Lewis acid activator. This invention also contemplates a process for producing a branched

10 polymer comprising:

contacting in the presence of a polymerization catalyst system,

(i) a macromonomer at least 250 carbons long comprising one or more C₂-C₃₀ olefinic monomer units

15 said macromonomer having chain end vinyl unsaturation, and

(ii) a polymerizable olefinic monomer or monomer mixture

under conditions to (co)polymerize the monomers

20 and incorporate the macromonomer into the growing (co)polymer chain via the chain end unsaturation,

said catalyst system comprising mono-, di-, or tri- cyclopentadienyl transition metal catalyst cocatalized with a non-coordinating anion, an aluminium

25 alkyl, or an alumoxane.

The reaction is maintained at 70°C, more preferably 70 to 100°C, even more preferably at 90°C. The weight ratio of macromonomer to olefin monomer present is between about 1:1 to about 1:5, preferably about 1:1.5

30 to about 1:3, more preferably about 1:2.

The branched polymers of this invention are comprised of a family of polyolefins and olefin copolymers which are copolymerizable by metallocene polymerization. Long chain branched polymers of this

35 type are made by copolymerization of vinyl terminated polymers with the desired ethylenically unsaturated monomer or monomers. The family of polyolefins

includes low to high density polyethylene or ethylene-alpha-olefin copolymers as well as polypropylene and polypropylene copolymers. The vinyl terminated polymers useful in this invention include high density polyethylene and polyethylene copolymers. Production of these polymers gives control over the side-chain molecular weight and composition. The branched polymers of this invention can be a low-density polyethylene with a high-density polyethylene branch. They are also not limited to side-chains consisting of the same polymer composition as the backbone. Likewise it is contemplated that the macromonomers can comprise homopolymers or copolymers of olefins, particularly of C₂ to C₃₀ alpha olefins. specifically a copolymer or polymer with more than 250 carbons that has vinyl termination can be used. The metallocene catalysts disclosed in this invention can produce vinyl-terminated homopolymers and copolymers. However, another method the produce vinyl termination is to produce a polymer with an ethylene "cap" or end with the needed vinyl group. This could be accomplished by raising the reaction temperature at the "end " of the reaction and simultaneously adding ethylene so that the ethylene pereferrientailly polymerizes to form an end "cap" or block. A block copolymer of ethylene and a C₃ to C₃₀ alpha olefin would also present the necessary vinyl termination.

The main chain and the sidechains may be the same of different olefin homo or copolymers. In particular main and side chains of ethylene are preferred. However main and side chains of ethylene copolymerized with propylene, 1-butene, 1-pentene, 4-methylpentene-1, 1-hexene or 1-octene are also preferred.

The ability to prepare long-chain branched olefins in which the side-chain compositions are significantly different from the backbone adds a unique dimension to the polymers of this invention

The branched polymers of this invention typically have a weight average molecular weight at or above 50,000, preferably 50,000 to 1,000,000 and a Mw/Mn of 6 or less. The vinyl terminated polymers (macromers) that become the side chains in the branched polymers of this invention are typically more than 200 carbons long, preferably 250 to 3500, even more preferably 300 to 3000 carbons long. Further these side chains insert into the main chain at an average of up to 5 side chains per 1000 main chain carbons, although it is statistically possible for a particular main chain to have no side chains. Also, as a benefit of utilizing titanium-containing monocyclopentadienyl transition metal catalysts in the catalyst system, a narrow composition distribution of the side chains may be obtained. A narrow composition distribution means that among the individual polymer main chains the number of side chains are roughly similar. For example, three main chains with 2, 3, and 2 side chains respectively have a very narrow composition distribution, while three main chains with 3, 9, and 20 sides chains, respectively, have a broad composition distribution. As an added benefit, if the main chain is a copolymer made using a titanium containing monocyclopentadienyl metallocene catalyst, it will have a narrow composition distribution and higher comonomer incorporation than traditional coordination catalysts.

It is also contemplated by this invention that the vinyl terminated macromonomer can be produced in one step of a continuous or series process which then proceeds to copolymerize the macromonomer with one or more alpha olefins. It is also contemplated that the macromonomer can be produced separately by one process and then polymerized later in a separate similar or different process.

CATALYSTS TO PRODUCE POLYMERS OF THE MACROMONOMER AND
AN OLEFIN

A large group of metallocene catalysts may be selected from to produce both the vinyl terminated
5 polymers (macromers) and the branched polymers of this invention. The choice of catalyst system is influenced by the characteristics desired in the final product. For example, a noncoordinating anion activation system rather than MAO could be found to be preferable to
10 avoid isomerization problems, or the metallocene catalyst Cp_2ZrMe_2 (bis cyclopentadienyl zirconium dimethyl) with $(\text{pfp})_3\text{B}$ (perflourotriphenyl boron) as the cocatalyst activator could be chosen because of this system's high activity at higher temperatures such
15 as 90°C and above. Further this catalyst system gives high levels of vinyl ends during polymerization in hexane and few or no vinyl ends when polymerized in toluene. The resulting vinyl terminated polymers are branched. This branching can be eliminated if a
20 sterically hindered catalyst like $(\text{Me}_5\text{Cp})_2\text{ZrMe}_2$ (bis pentamethylcyclopentadienyl zirconium dimethyl) is used. This catalyst system sterically inhibits the copolymerization of vinyl terminated polymers. It should be noted that the vinyl terminated macromonomers
25 of this invention can be branched. However the level of this branching does not approach a dendritic structure. These macromers and those that have little or no side chain branching or are substantially linear will be referred to as linear.

30 The catalyst choices for copolymerization of vinyl terminated polymers with other monomers are also large and include catalyst systems containing bridged and unbridged bis cyclopentadienyl transition metal compounds as well as monocyclopentadienyl transition
35 metal compounds. Monocyclopentadienyl transition metal catalysts are preferred as they polymerize large "monomers" well. For example, monocyclopentadienyl

(Mono Cp) transition metal catalysts, particularly titanium, incorporate more monomer than coordination catalysts. Thus one would choose a Mono Cp Ti catalyst to make lower density products over the

- 5 Tris(perfluorophenyl)Boron activated systems utilized in example 1 and 2 to make high density material.

To understand the advantages of polymers produced in accordance with the present invention, some general discussions of the properties of polymer solids and
10 melts is helpful. Molten polyethylene is highly viscous. The viscosity is a function of weight-average molecular weight (M_w); molecular weight distribution (M_w/M_n), also called the index of polydispersity; and the shear rate exerted on the polymer. The molecular
15 weight values are in part related to branching of the polymer. Molten polyethylene is classified as a pseudoplastic fluid, which means that its viscosity decreases with increasing shear rate. The relationship between viscosity and shear rate depends upon the
20 molecular weight distribution and degree of long chain branching of the polymer. Polymers having a broad molecular weight distribution tend to have lower viscosity values at conditions of high shear rates than polymers having a narrow molecular weight distribution
25 while having equivalent viscosities at conditions of low shear rates.

As noted, viscosity as a function of shear rate is also dependent upon the degree of long chain branching of a polymer which affects molecular weight
30 distribution. In general, a polymer with long chain branching will have higher viscosity values at low shear rates and lower viscosity values at high shear rates compared to an unbranched polymer with equivalent molecular weight. Lower viscosity at high shear rates
35 means the long chain branched polymer can be extruded at lower temperatures and at a higher rate which results in less energy consumption.

From a processability viewpoint, it is usually desirable to have a polymer which displays high viscosity at low shear rates and low viscosity at high shear rates, in other words, it is desirable to have a polymer that processes with the characteristics of a branched polymer at conditions of low shear while having the processing characteristics of a broad molecular weight distribution branched polymer at conditions of high shear. This combination of properties is often sought by broadening the molecular weight distribution of a polymer by introducing long chain branching.

The inventors have found that the positive viscosity processing characteristics of a polymer at both ends of the shear rate range may be achieved by polymers in accordance with the present invention. The predictable solid polymer mechanical properties achievable by polymers in accordance with the present invention are good impact and tear resistance, good environmental stress crack resistance (ESCR) values, good tensile properties, good modulus/density balance, good reblock/density balance, and good clarity, relative to linear polyethylenes without long chain branching.

This unique balance of favorable polymer melt processability and solid polymer mechanical characteristics is achieved through the creation of remote long chain branching at a frequency and length great enough to impart processability characteristics of LDPEs but at a low enough frequency so as not to destroy the superior solid polymer physical characteristics of LPEs. In particular, this balance is achieved by the introduction of some linear long chain branches having a average molecular weight greater than the critical molecular weight for entanglement (M_c) of the polymer with a linear long chain branching frequency less than 5.0 branches per

1,000 carbon atoms of the main polymer chains. These polymers may be produced over a wide range of molecular weight distributions (M_w/M_n) (index of polydispersity) of 2.0 to 10. Preferably, the frequency of long chain branching is less than 5 branches per 1,000 carbon atoms of the main polymer chains (preferably an average frequency of 0.2 to 3 chains per 1000 C, atom, even more preferably an average frequency of 0.9 to 2 chains per 1000 C, even more preferably an average frequency of 1 to 2 chains per 1000 C) with a preferred molecular weight distribution range of about 2 to about 6, more preferably 2 to 4.

These advantageous properties can be achieved when even 5 or more weight percent of the composition is "branched." This may occur when a branched polymer is blended with another polymer or when the branched polymer is part of a reactor blend. Preferably the branched polymer is present at least 5 weight percent, even more preferably at least 10 weight percent, even more preferably at least 40 to 70 weight percent.

The viscosity characteristics of polymers of the present invention are not the only processing advantages. Another advantage of polymers having linear long chain branching in accordance with the present invention are the superior elastic characteristics of the polymer melt. Molten polyethylene exhibits elastic properties over a wide temperature range. After molten polyethylene passes through the die of an extruder under pressure, the strand of polyethylene increases in diameter or thickness. This is known as extrudate swell. At low shear rates, extrudate swell increases as molecular weight and long chain branching increase. In other words, extrudates typically swell as molecular weight distribution broadens.

Polymers produced in accordance with the present invention exhibit increased extrudate swell. The

significance of this increased extrudate swell is that is a reflection of what is known as the elastic nature of the polymer. The elastic nature of the polymer is very important in certain polymer melt extrusion processes such as the manufacture of tubular film, chill roll casting and extrusion coating in which an extruded web of film is produced which is stretched in the direction of flow. Such extrusion processes can only be carried out with materials that are able to sustain a tensile stress on the melt. In other words, it is important that the polymer melt be somewhat elastic. There should be a balance between the elasticity of the polymer melt and the viscosity in blow molding operation. The balance between elasticity and viscosity of the polymer melt affects parison integrity. If the balance of properties is in favor of viscosity over elasticity, the polymer melt will not have good stability and tend to sag during certain extrusion processes. There is a strong correlation between extrudate swell ratios and parison integrity. The introduction of long chain branching in accordance with the present invention results in polymer melts having swell ratios indicative of good elastic properties for extrusion processes.

The presence of a small amount of long chain branching in a linear molecule increases elasticity of the polymer melt by introducing very long relaxation times in the relaxation spectrum of the melt. Since the polymer melt is a collection of molecules with different lengths and different branches, each molecule will respond differently to a given deformation. The collection of response times is referred to as the relaxation time spectrum which directly relates to the stability of the polymer melt during extrusion.

Long chain branching in accordance with the present invention has another important advantage of changing the elongational characteristics of polymer

melts. The presence of long chain branching increases the value of the longational viscosity and introduces a maximum elongation viscosity as a function of strain rate.

5 The polymers produced in accordance with the present invention have still another advantage of having a reduced tendency to melt fracture at high shear rates. Smooth extrudates of polymer melts may be obtained easily at low shear rates. However, above a
10 critical shear rate, the extrudate becomes uneven. The form of distortion of the extrudate varies. In some cases, the extrudate has the form of a screw thread, in others, the extrudate becomes spiral twisted while in others the distortion may take on the affect of a
15 regular ripple or even random distortions. The critical shear rate of a polymer is related to the degree of entanglement of the polymer. The greater the degree of entanglement of the polymer, the lower the critical shear rate. Since the polymers produced in
20 accordance with the present invention, due to the linear long chain branching, have less entanglement than linear polymers, the critical shear rate of these polymers will be increased. The result is that
25 polymers made in accordance with the present invention have a reduced tendency to melt fracture at high shear rates than conventional linear polymers.

 The polymers of the present invention also enjoy the good solid polymer mechanical properties associated with short chain branching distributions of single
30 site catalyst polymerizations. The polymers produced in accordance with the present invention may have high molecular weights with narrow molecular weight distributions. These narrow distributions result in products having lower extractables caused by amorphous
35 waxes, better clarity due to the absence of large light refracting crystals, and superior impact resistant due

to increased number of tie molecules binding crystal regions together.

The frequency of chain branching is determined by ^{13}C NMR spectrometry for homopolymers and by measuring
5 the viscous energy of activation of copolymers with a parallel plate oscillating shear melt rheometer.

Long chain branching may be detected by comparing the results of different gel permeation chromatography (GPC), measured with both a refractive index detector
10 and a low angle laser light scattering detector. GPC separations are governed by the hydrodynamic volume of polymeric molecules in solution. The standard detector on most GPCs measures the relative refractive index (RI) of the effluent. The RI detector assumes that
15 molecules coming off the separation column at Time 1 have the same molecular weight as molecules eluting from an unbranched calibration standard at Time 1. It has been discovered that long chain branches do not increase the hydrodynamic volume of a molecule by an
20 amount proportional to the length of its branches. It is believed that the contribution in the hydrodynamic volume is only a fraction of the branch length. In other words, refractive index detectors cannot "see" linear long chain branches in accordance with the
25 present invention. However, a low angle light scattering (LALLS) detector does "see" all carbons in a polymer molecule. By analyzing a sample with both detectors, the difference in the results provides evidence of long chain branching in accordance with the
30 present invention. This technique is illustrated by the following data:

	Sample	Mw	Mw
		(DRI detector)	(LALLS detector)
.35	A	99800	99900
	B	111000	116000
	C	206000	231000

Sample A is an ethylene-hexene copolymer made in a gas phase process with a metallocene catalyst which is known to have no long chain branches. By comparing the molecular weight values calculated by the standard refractive index detector (RI) and the LALLS detection method, one sees that there is no significant difference in the values suggesting there are no hidden branches. Comparing the RI and LALLS values for sample B, an increase of 5,000 in molecular weight is seen by the LALLS detection method. With sample C, a 25,000 molecular weight increase is detected. The higher molecular weight of samples B and C as determined with the LALLS detector are evidence of long chain branching.

By comparing the different GPC techniques for polymers in accordance with the present invention, one generally sees that molecular weight as calculated by the LALLS technique is greater than the molecular weight as calculated by the RI GPC technique.

Long-chain branching in polyethylene is defined as those branches which produce one or more of the following effects.

1. High viscous energy of activation (Ea).

Polymer viscous energy of activation can be determined with parallel plate shear melt rheometry. Melt viscosity-temperature dependence is determined by performing shear rate superposition. The resulting shift factors are fitted to an Arrhenius equation; the product is the viscous energy of activation.

The energies of activation for a variety of polyethylene types are illustrated in the bar chart of figure 1. HDPE represents narrow MWD, linear homopolymers in the 5-50 MI range. LLDPE represents narrow MWD, linear ethylene-butene copolymers with comonomer content ~12% and MI in the 1-2 dg/min range. HMW-HDPE represents narrow MWD, linear ethylene

homopolymers with Mw's greater than 200k (i.e., MI < 0.2 dg/min). LDPE represents long-chain branched, ethylene homopolymers produced in a free-radical process. The LPE w/ LCB represents some of the branched polymers of this invention.

The unusually high Ea of the LPE w/ LCB is clear evidence of long-chain branching.

2. Low viscosity, moderate shear rates relative to unbranched NMWD linear polymers.

Melt viscosities can be measured vs. shear rate with a capillary rheometer. Figure 2 is an illustration of the relationship between the Mw of NMWD linear polyethylenes, and their melt viscosity measured at 340 s⁻¹ and 190°C. This data is narrowly distributed about a linear model: viscosity = 0.0115 x Mw - 325. The position of the LDPE samples reflects the known fact that LDPEs are more "shear thinning" than linear polyethylenes, i.e., their viscosities decrease more rapidly as shear rate increases than do the viscosities of linear polyethylenes. The position of the LPE w/ LCB is clear evidence that this NMWD linear homopolymer contains long-chain branching. The branched polymers of this invention have a viscosity measured at 340sec-1/190°C of 0.75(0.0115 x Mw - 325).

3. High melt strength.

Melt strength can be determined with a Rheotens Instrument which consists of a capillary rheometer equipped with an accelerating wheel take-off station. The melt tensile force in the capillary rheometer extrudate is measured as a function of the instantaneous wheel velocity. Figure 3 illustrates the relationship between melt tension, measured at 190°C immediately before the onset of severe draw resonance, and Mw for numerous unbranched, narrow MWD linear ethylene-alpha-olefin copolymers. These tensile forces

are narrowly distributed about a linear model: melt
tensile force = $(7.68 \times 10^{-5}) \times Mw - 4.32$. The
branched polymers of this invention will exhibit a melt
tensile force of $1.3((7.68 \times 10^{-5}) \times (Mw \text{ of the}$
5 polymer) - 4.32).

The unusually high tensile force observed with the
LDPE is attributed to its long-chain branching.
Evidence of the maximum frequency of the long-chain
branches in a linear polymer can be determined with
10 carbon-13 NMR if the polymer contains no short-chain
branches, due to the comonomer, which are larger than 3
carbons in length. The carbon atom in the polymer's
backbone to which a branch, which is larger than 3
carbons in length, is attached produces a signal in the
15 C13-NMR spectrum at 38 ppm, which is distinguishable
from all other carbons in the qualifying test sample
and therefore a measure of the maximum number of long-
chain branch points.

The present invention may be illustrated by the
20 following examples:

EXAMPLE 1 Macromer A

A one liter autoclave solution polymerization
reactor was charged with 400 ml toluene, 40 psig
25 ethylene, and 58.9mg Cp_2ZrMe_2 & 11mg B(pfp)₃
[Bis(cyclopentadienyl)Zirconiumdimethyl & tris
(pentafluorophenyl) Boron]]. The mixture was reacted at
90°C (16° exotherm) for 0.87 hours. The polymerization
yielded 121.4 grams of polymer after drying in a vacuum
30 oven for 24 hours until odor-free. The dried polymer
consisted of irregularly-shaped particles ranging in
size from less than 0.1 mm to greater than 1 cm. The
density of the polymer was 0.953 g/cm³, with a weight-
average molecular weight (M_w) of 29,000 with a level of
35 vinyl that was not detected by NMR, and an index of
polydispersity (M_w/M_n) of 3.28. The polymer had a
chain branching frequency of 0.48 branches per 1,000

carbon atoms of the main polymer chains by ^{13}C NMR analysis.

EXAMPLE 2 Polymerization with Macromer A

5 A one liter solution polymerization autoclave reactor was charged with 400ml toluene, 25g of macromer A produced in example 1 (linear ethylene homopolymer having a weight-average molecular weight (M_w) of 29,000 with very low levels, i.e. not detected, of vinyl
10 unsaturations per 1,000 carbon atoms) and 100 psig ethylene, and 0.24 millimoles of bis (cyclopentadiene) dimethyl zirconium tris (pentafluorophenyl) boron catalyst (in toluene) with an initial reactor temperature of 45°C. The solution temperature was
15 raised to 102°C and reacted for 0.33 hours. The polymerization yielded 57.0 g of polymer after drying in a vacuum oven for 24 hours until odor-free. The dried polymer consisted of irregularly-shaped particles ranging in size from less than 0.1 mm to greater than
20 1.0 cm. The density of the polymer was 0.953 g/cm³, with a weight-average molecular weight (M_w) of 82,500 and an index of polydispersity (M_w/M_n) of 5.3 The polymer had a long chain branching frequency of 2 long chain branches per 1,000 main chain carbon atoms by ^{13}C
25 NMR analysis.

EXAMPLE 3 Macromer B

A one liter autoclave solution polymerization reactor was charged with 400 ml of hexane, 20 psig
30 ethylene, and 60 mg of bis (cyclopentadiene) dimethyl zirconium catalyst and 60 mg of tris (pentafluoronyl) boron catalyst activator. The mixture was reacted at 90°C for 0.7 hours. The polymerization yielded 26g of polymer after drying in a vacuum oven for 24 hours
35 until odor-free. The weight-average molecular weight (M_w) of the polymer was 21,000 and the index of polydispersity (M_w/M_n) was 8.2. The polymer had a

chain branching frequency of 1.22 branches per 1,000 main chain carbon atoms of the main polymer chains by ^{13}C NMR analysis.

5 EXAMPLE 4 Polymerization with Macromer B

A one liter autoclave solution polymerization reactor was charged with 400ml of toluene, 25g macromer B produced in example 3 (linear ethylene homopolymer having a weight-average molecular weight (M_w) of 21,000 and 1.0 vinyl unsaturations per 1,000 carbon atoms) and 50 psig ethylene, and 0.24 milimoles bis (cyclopentadiene) dimethyl zirconium tris (pentafluorophenyl) boron catalyst (in toluene). The mixture was reacted at 60°C (42° exotherm) for 0.28 hours. The polymerization yielded 78.8g of polymer after drying in a vacuum oven for 24 hours until odor-free. The weight-average molecular weight (M_w) was 32,000 and index of polydispersity or MWD, (M_w/M_n) was 3.0. The polymer had a linear long chain branching frequency of 0.48 branches per 1,000 carbon atoms of the main polymer chains by ^{13}C NMR analysis.

CLAIMS

What is claimed is:

1. A branched polyolefin comprising:
 - a main chain (b) of a homopolymer or a
5 copolymer of C₂ - C₃₀ alpha olefins; and
 - side chains (a) of at least 250 carbon atoms
comprising a homopolymer or a copolymer of C₂ -
C₃₀ alpha olefins, said side chains being
distributed along the polymer main chain at an
10 average frequency of 0.1 to 5 side chains per 1000
main chain carbon atoms,
said branched polymer having a weight average
molecular weight of at least 30,000 and an M_w/M_n
of 6 or less.
- 15 2. The branched polyolefin of claim 1 wherein the side
chains(a) are 300 to 3000 carbons long.
3. The branched polyolefin of claim 1 or 2 having a M_w
20 of 30,000 to 1,000,000.
4. The branched polyolefin of any previous claim
having a M_w/M_n between 1 and 4.
- 25 5. The branched polyolefin of any previous claim
having side chains(a) present at an average frequency
of 0.2 to 3 side chains per 1000 main chain carbons.
6. The polyolefin of any previous claim wherein the
30 side chains (a) derive from ethylene and any C₃ to C₃₀
alpha olefin and the main chain, independently, derives
from ethylene and any C₃ to C₃₀ alpha olefin.
7. The branched polymer of any previous claim
35 characterized by a density of 0.85 to 0.95g/cm³.

8. The branched polymer of any previous claim wherein the side chains (a) comprise block copolymer of ethylene and propylene.

5 9. The polymer of any previous claim wherein the side chains (a) comprise a polymer of any C₃ to C₃₀ alpha olefin with an ethylene block present at the insertion point along the main chain.

10 10. A polymer blend composition comprising at least 5 weight percent, based upon the weight of the composition, of a branched polyolefin of any previous claim.

15 11. A film or article of manufacture comprising the branched polymer of any previous claim.

12. A method for producing polyolefins of claims 1-10 comprising the steps of:

- 20 1) contacting under polymerization conditions :
one or more alpha olefin monomers with a catalyst system to produce a vinyl terminated macromonomer of at least 250 carbon atoms long;
- 25 2) subsequently contacting, under polymerization conditions:
said vinyl terminated macromonomer; with one or more alpha olefin monomers; and a catalyst system comprising a cyclopentadienyl transition metal catalyst and a cocatalyst or
- 30 activator.

13. The method of claim 12, wherein the transition metal is Zr, Hf, or Ti.

14. The method of claims 12 or 13, wherein the cocatalyst activator is an alumoxane or a Lewis acid activator.

5 15. The method of claims 12, 13, or 14 wherein the polymerization conditions for step 2) are solution, gas phase, bulk phase, or supercritical phase polymerization conditions.

10 16. A branched polyolefin of claim 1 having energy of activation greater than about 9 kcal/mole or a viscosity of $0.75X(0.0115 \times Mw \text{ of the polymer } -325)$ and a melt strength $1.3x((7.68 \times 10^{-5}) \times Mw-4.32)$.

15 17. The method of claims 12 - 15, wherein the cyclopentadienyl transition metal catalyst is a transition metal compound comprising a single cyclopentadienyl group and a heteroatom containing group each bonded to the transition metal, said
20 cyclopentadienyl group and heteroatom containing groups optionally bridged through a divalent moiety.

INTERNATIONAL SEARCH REPORT

Inter. Appl. Application No

PCT/US 93/08833

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08F299/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO,A,91 17194 (EXXON CHEMICAL PATENTS) 14 November 1991 see page 9, line 20 - line 26 see page 12, line 1 - line 28 ---	1
A	EP,A,0 366 411 (EXXON CHEMICAL PATENTS) 2 May 1990 ---	1
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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INTERNATIONAL SEARCH REPORT

Inter. Application No
PCT/US 93/08833

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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information on patent family members

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